

PATENT ABSTRACTS OF JAPAN

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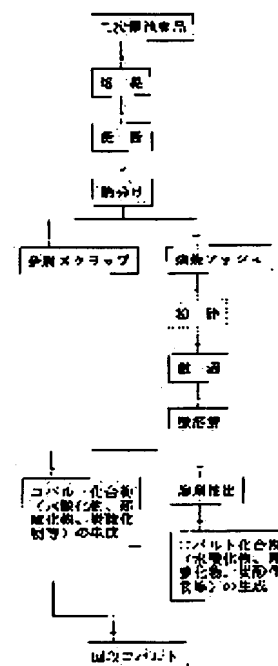
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(54) METHOD FOR RECOVERING COBALT FROM SPENT SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for recovering cobalt from a spent secondary battery by which a cobalt as a rare metal is efficiently recovered from a spent secondary battery by the use of acid in an amt. as small as possible.

SOLUTION: A spent secondary battery contg. cobalt in its electrode material is roasted at $\geq 600^{\circ}\text{C}$, the roasted battery is cut to pieces, and the pieces are screened into metallic scraps and roasted ash. A cobalt-contg. material is magnetically separated from the ash with a magnet, and the cobalt-contg. material is dissolved in an acid to recover cobalt from the acid soln.



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CLAIMS

[Claim(s)]

[Claim 1] The roast process which roasts over the temperature of 600 degrees C or more the cell useless article of the rechargeable battery which contains cobalt in electrode material, The decision process which cuts out the roast cell obtained at this roast process, and the sieving process which sifts out the decision object of the roast cell obtained at this decision process, and is divided into a metal scrap and a roast ash, The magnetic separation process which carries out the magnetic separation of the cobalt inclusion using a magnet out of the roast ash obtained at this sieving process, The cobalt recovery approach from the rechargeable battery useless article characterized by including the acid dissolution process of dissolving the cobalt inclusion sorted out at this magnetic separation process in an acid, and the recovery process which collects cobalt from the acid melt obtained at this acid dissolution process.

[Claim 2] The cobalt recovery approach from a rechargeable battery useless article according to claim 1 that a recovery process is a solvent extraction process which collects cobalt by solvent extraction.

[Claim 3] The roast of the cell useless article in a roast process is the cobalt recovery approach from the rechargeable battery according to claim 1 or 2 performed at the temperature of 700-900 degrees C in a well-closed container or reducing atmosphere.

[Claim 4] The roast ash obtained at the sieving process is the cobalt recovery approach from a rechargeable battery useless article given in any of claims 1-3 ground by predetermined grain size before magnetic separation is carried out at a magnetic separation process they are.

[Claim 5] A roast ash is the cobalt recovery approach from a rechargeable battery useless article given in any of claims 1-4 ground by the average grain size of 2mm or less they are.

[Claim 6] The magnetic separation of the roast ash in a magnetic separation process is the cobalt recovery approach from the rechargeable battery useless article given in any of claims 1-5 they are performed according to wet magnetic separation.

[Claim 7] the cobalt inclusion sorted out at the magnetic separation process -- the roast ash in front of magnetic separation -- receiving -- a weight ratio -- the cobalt recovery approach from a rechargeable battery useless article given in any of claims 1-6 which are 0.6 or less they are.

[Claim 8] The roast process which roasts over the temperature of 600 degrees C or more the cell useless article of the rechargeable battery which contains cobalt in electrode material, The decision process which cuts out the roast cell obtained at this roast process, and the magnetic separation process which carries out the magnetic separation of the decision object of the roast cell obtained at this decision process to the magnetic substance and non-magnetic material with a magnet, The sieving process which sifts out the magnetic substance obtained at this magnetic separation process, and is divided into a magnetic metal scrap and a cobalt inclusion, The cobalt recovery approach from the rechargeable battery useless article characterized by including the acid dissolution process of dissolving the cobalt inclusion obtained at this sieving process in an acid, and the recovery process which collects cobalt from the acid melt obtained at this acid dissolution process.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the cobalt recovery approach that the cobalt of the rare metal contained in that electrode material is efficiently recoverable from cell useless articles, such as a defective generated in the production process of a rechargeable battery, and a recovery article of a used rechargeable battery, from a rechargeable battery useless article.

[0002]

[Description of the Prior Art] For example, lithium acid cobalt (LiCoO_2) is used for the rechargeable lithium-ion battery as the positive-electrode material, and cobalt oxide is added by the nickel hydride battery for the purpose of the improvement in a capacity utilization factor in the hydrogenation nickel which is the active material of the positive-electrode material, and the cobalt nitrate is further added by the nickel-cadmium battery for the purpose of corrosion-resistant improvement or high-capacity-izing in the positive-electrode material (nickel).

[0003] Such positive-electrode material and in the case of a rechargeable lithium-ion battery Mix and calcinate a lithium carbonate and cobalt oxide and it considers as lithium acid cobalt. Subsequently, an electric conduction agent and fluororesins, such as this lithium acid cobalt, acetylene black, carbon, etc., Blend binders, such as a fluororubber, and this is kneaded in the shape of a slurry with an organic solvent. this kneading object -- a metallic foil top, such as aluminium foil (only henceforth "aluminum foil"), -- homogeneity -- applying -- drying -- a solvent -- removing -- a metallic foil -- an electric conduction agent -- 2 - 10 % of the weight and 2 - 10 % of the weight of binders are applied, and it is formed by judging this in a predetermined configuration.

[0004] By the way, the amount of cell useless articles, such as a defective generated at the time of manufacture of this rechargeable battery and a recovery article of a used rechargeable battery, increases by leaps and bounds, and processing of these cell useless article is becoming a problem as need increases quickly with the spread of portable electrical machinery and apparatus, such as a notebook sized personal computer, cellular-phone, simple cellular-phone (PHS), and electrical-and-electric-equipment shaver, a headphone stereo cassette tape recorder, and VTR, and that volume increases such a rechargeable battery.

[0005] In spite of cobalt's being poor in a resource and depending for the most on a foreign country in our country on the other hand, the application is continuing very extensively until it results [from daily necessities, such as the electrode material of a rechargeable battery, a pigment, a ceramic industry, a ferrite a catalyst, and cemented carbide,] in a high-tech product, and is used especially for the rechargeable lithium-ion battery about 7g as cobalt oxide per the one individual. For this reason, that need grows and cobalt is becoming still more expensive while it is expensive from the first.

[0006] For this reason, also in the former, acid dissolution processing of the trash of cemented carbide or a catalyst is carried out, for example. Cobalt ion is alternatively extracted from the acid solution containing the cobalt and nickel which were obtained in this extractant by the extractant containing alkyl phosphoric acid. Furthermore, by contacting the obtained extract in an oxalic acid water solution, depositing oxalic acid cobalt, and collecting, the method of collecting cobalt from the solution containing cobalt and nickel by the high grade is proposed (JP,5-14013,B).

[0007]

[Problem(s) to be Solved by the Invention] Then, grinding this, dissolving by mineral acids, such as a hydrochloric acid and a nitric acid, also about the cell useless article mentioned above, carrying out separation removal of the binders, such as electric conduction agents, such as insoluble acetylene black and carbon, and a fluororesin, a fluororubber, etc., collecting the acid solutions containing metals, such as

lithiums including cobalt and aluminum, and collecting cobalt alternatively by the extractant which contains alkyl phosphoric acid from this acid solution is examined.

[0008] However, in this approach, since metallic compounds, such as cobalt in a cell useless article and a lithium, not only dissolve into an acid solution, but it dissolves including the aluminum of a metallic foil etc. The amount of the acid which the amount of a cell useless article takes for increasing, and this acid dissolution processing takes to it, for example, a hydrochloric acid, the nitric acid used, etc. increases sharply. The acid waste fluid after extracting cobalt ion from this acid solution by extractant arises in large quantities. A lot of alkali, such as a sodium hydroxide, is needed for processing of these acid waste fluid of a lot of, and a problem great to waste fluid processing on the contrary occurs, and also If a hydrochloric acid is used as an acid, chlorine gas will occur in large quantities at the time of acid dissolution processing, and if a nitric acid is used, a nitrogen peroxide will occur in large quantities at the time of acid dissolution processing, and there is also a problem that processing of these acid exhaust gas also takes great costs.

[0009] Moreover, first, dissolve in alkali, such as a sodium hydroxide, and metallic foils, such as aluminum foil in a cell useless article, some lithium compounds, etc. are removed. Next, other metallic compounds, such as a cobalt compound in the left-behind positive-electrode material, an electric conduction agent, Acid dissolution processing of the binder etc. is carried out by mineral acids, such as a hydrochloric acid, positive-electrode material, and the electric conduction agent and binder of fusibility are separated, and the method of collecting cobalt alternatively by the extractant which obtains the acid solution containing metals, such as cobalt and a lithium, and contains alkyl phosphoric acid is also considered.

[0010] However, in this approach, alkali pretreatment for carrying out separation removal of the metallic foil by alkali apart from acid leach processing is needed, a process is complicated, the alkali waste and the acid waste fluid which were further used by these alkali pretreatment or acid leach processing are generated in large quantities, like the above, a great problem occurs in waste fluid processing, and also the acid exhaust gas problem at the time of acid leach processing remains.

[0011] Furthermore, the approach of carrying out the direct solution extract of the cobalt alternatively is indicated from cobalt and a nickel oxide by using the organic solution containing alkyl phosphoric acid for JP,3-10032,A under existence of water.

[0012] However, in this approach, even if metallic compounds, such as a cobalt compound, are covered by the electric conduction agent and the binder in positive-electrode material, existence of this electric conduction agent and binder becomes a failure, and extractant of the organic solution-drainage system containing alkyl phosphoric acid cannot contact a cobalt compound and an effectiveness target but the extraction efficiency by this extractant is high, it is not the value which it is low and can simply be industrially carried out with about 30 - 40 % of the weight.

[0013] Then, the result of having repeated research wholeheartedly about how this invention persons separating and collecting the cobalt of a rare metal from a cell useless article, Magnetic separation of the cobalt inclusion which uses metal cobalt and cobalt oxide as a principal component for the roast ash which carried out roast processing above 600 degrees C, subsequently cut out the cell useless article, sifted out, and was obtained using a magnet is carried out. A header and this invention were completed for moreover cobalt being efficiently recoverable, without having carried out acid dissolution processing of the obtained cobalt inclusion, and using a lot of acids for the cobalt in a cell useless article by carrying out solvent extraction processing.

[0014] Therefore, the purpose of this invention is to offer the cobalt recovery approach from a rechargeable battery useless article that the cobalt of a rare metal is efficiently recoverable from the cell useless article of a rechargeable battery using a small amount of as much as possible acid.

[0015]

[Means for Solving the Problem] Namely, the roast process which roasts over the temperature of 600 degrees C or more the cell useless article of the rechargeable battery with which this invention contains cobalt in electrode material, The sieving process divided into the decision process which cuts out the roast cell obtained at this roast process, and the roast ash which sifts out the decision object of the roast cell obtained at this decision process, and contains a metal scrap and a cobalt inclusion, The magnetic separation process which carries out the magnetic separation of the cobalt inclusion using a magnet out of the roast ash obtained at this sieving process, It is the cobalt recovery approach from a rechargeable battery useless article including the acid dissolution process of dissolving the cobalt inclusion sorted out at this magnetic separation process in an acid, and the recovery process which collects cobalt from the acid melt obtained at this acid dissolution process.

[0016] Moreover, the roast process which roasts over the temperature of 600 degrees C or more the cell

useless article of the rechargeable battery with which this invention contains cobalt in electrode material, The decision process which cuts out the roast cell obtained at this roast process, and the magnetic separation process which carries out the magnetic separation of the decision object of the roast cell obtained at this decision process to the magnetic substance and non-magnetic material with a magnet, The sieving process which sifts out the magnetic substance obtained at this magnetic separation process, and is divided into a magnetic metal scrap and a cobalt inclusion, It is the cobalt recovery approach from a rechargeable battery useless article including the acid dissolution process of dissolving the cobalt inclusion obtained at this sieving process in an acid, and the recovery process which collects cobalt from the acid melt obtained at this acid dissolution process.

[0017] In this invention approach, the rechargeable battery useless article set as the object of cobalt recovery is a defective, a recovery article of a used rechargeable battery, etc. which are generated at the time of manufacture of a rechargeable battery, and contains cobalt in electrode material. The rechargeable lithium-ion battery which contains cobalt compounds, such as cobalt oxide and a cobalt nitrate, etc. in that positive-electrode material typically as a rechargeable battery which contains cobalt in this electrode material, a nickel hydride battery, a nickel-cadmium battery, etc. can be mentioned.

[0018] In this invention approach, 600 degrees C or more of cell useless articles of the rechargeable battery which contains cobalt in electrode material in this way first are usually preferably roasted over the temperature of 700-900 degrees C for about 1 to 3 hours. Some cobalt compounds in electrode material are returned at least, and roast processing at the roast process of this cell useless article needs to serve as metal cobalt, in order to carry out the magnetic separation of the cobalt inclusion which is preferably performed in a well-closed container or reducing atmosphere, and uses metal cobalt and cobalt oxide as a principal component at a magnetic separation process efficiently. Here, if roast temperature is lower than 600 degrees C, the amount of the metal cobalt in the cobalt inclusion in the roast ash obtained will decrease, and it will become difficult to carry out the magnetic separation of the cobalt inclusion efficiently at a magnetic separation process. Moreover, even if roast temperature exceeds 900 degrees C, it is not desirable, although there is especially no problem in sorting of the cobalt inclusion in a magnetic separation process, and the energy cost in a roast process increases and being carried out industrially.

[0019] At this roast process, for example The cobalt oxide in the positive-electrode material of a cell useless article While aluminum (aluminum), carbon (C), etc. in this cell useless article are returned to (for example, Co_2O_3) as a reducing agent, and that part is returned completely and changing into the metal cobalt (Co) of the magnetic substance It is thought that the cobalt oxide (Co_3O_4) which it was partially returned and was generated exists with this metal cobalt.

[0020] The roast cell obtained at the above-mentioned roast process is cut out with a cutter next, and serves as a decision object. In the decision object of this roast cell The comparatively big metal scrap of the piece of decision originating in the charge collector formed by metallic foils, such as an outside container of the cell formed with metals, such as iron, aluminum, and stainless steel, and aluminum foil, copper foil, The electric conduction agent and fluororesins with which the charge collector was plastered, such as metallic compounds, such as a cobalt compound, acetylene black, and carbon, The comparatively small roast ash of powdered or granularity which consists of a metal of the metal cobalt originating in organic substances, such as a separator formed by positive-electrode material, such as binders, such as a fluororubber, negative-electrode material, the polyethylene porosity film, etc., etc., cobalt oxide, and others, the oxide, carbon, etc. exists.

[0021] And the decision object of the roast cell obtained at the above-mentioned decision process Sift out previously, and at a process, it is sifted out by the metal scrap of the comparatively big piece of decision, and the comparatively small roast ash of powdered or granularity, and separates into them. Subsequently, although the cobalt inclusion of the magnetic substance is sorted out at a magnetic separation process, or the magnetic substance and non-magnetic material sort out with a magnet at a magnetic separation process previously, it subsequently sifts out, the magnetic substance is sifted out at a process and it separates into a magnetic metal scrap and a cobalt inclusion While reducing the throughput in a magnetic separation process, in order to separate a metal scrap and a roast ash more completely, after sifting out at the former point preferably, it is the approach of carrying out magnetic separation.

[0022] At the above-mentioned sieving process, a vibration screen is used preferably, the roast ash adhering to a metal scrap is removed as much as possible, and the collected metal scrap, for example, iron, stainless steel, aluminum, and copper are recycled and used effectively. Moreover, especially at the above-mentioned magnetic separation process, although not restricted, magnetic separation are performed using the difference of the adhesion time amount of the quality of a magnetic matter, and the nonmagnetic matter, for example

using equipments, such as a drum-type wet separator, and a belt mold wet separator, a dry separator of further various types.

[0023] It is good to carry out grinding processing with grinders, such as a ball mill, as occasion demands, and to grind the grain size of this roast ash below to 1.168mm (16 meshes) more preferably below 1.651mm (12 meshes) here the average grain size of 2mm or less about the roast ash obtained at the sieving process, before transporting this to a magnetic separation process. Thus, by grinding a roast ash in average grain size of 2mm or less, it is divided into the fine particles which contain comparatively in high concentration a metal other than the fine particles which contain metal cobalt and cobalt oxide in high concentration comparatively, and cobalt, and its oxide, and the cobalt inclusion which contains metal cobalt and cobalt oxide in high concentration comparatively at a magnetic separation process is obtained.

[0024] The cobalt inclusion sifts out from a magnetic separation process and pass the process through a sieving process to a magnetic separation process Although the effectiveness of the amount of the acid used needed by next acid dissolution processing decreasing so much, and making the amount of the acid used at an acid dissolution process decreasing will be acquired if the weight is decreasing to the roast ash in front of the magnetic separation which cut out the roast cell and was produced when making the amount of the acid used at this acid dissolution process decrease as much as possible often carries out industrially -- desirable -- the roast ash in front of magnetic separation -- receiving -- a weight ratio -- it is [0.6 or less] good to carry out to 0.5 or less more preferably.

[0025] Although the cobalt inclusion obtained at this magnetic separation process uses metal cobalt and cobalt oxide as a principal component, it contains for example, metal cobalt, and metals and the oxide of those, such as sintered copper and aluminum, at a considerable rate in addition to these. As for the metal cobalt in this cobalt inclusion, and the content rate (this is only hereafter called "cobalt content") of the sum total of cobalt oxide, it is usually preferably good that it is 40 % of the weight or more 20% of the weight or more. The more this cobalt content is high, the amount of the acid needed to the amount of unit cobalt decreases, and, the more the amount of the acid used in an acid dissolution process decreases.

[0026] In this invention, suitable acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, are used for the cobalt inclusion obtained at the magnetic separation process next, it dissolves, and let it be an acid melt (acid dissolution process). As an acid used at this acid dissolution process, mineral acids, such as a hydrochloric acid and a sulfuric acid, are mentioned typically, and the range of that amount used is usually 1-3 mols to one mol of cobalt inclusions.

[0027] The acid melt obtained at the acid dissolution process is transported to the recovery process for next collecting cobalt. About this recovery process, that what is necessary is just the process at which it can collect cobalt from an acid melt alternatively For example, after carrying out separation removal of the metallic compounds other than a cobalt compound as much as possible by pH adjustment, The approach of adjusting to pH10, depositing cobalt hydroxide, returning this cobalt hydroxide in reducing atmosphere, and collecting as metal cobalt, the approach (JP,56-11371,B --) of carrying out liquid-liquid extraction of the cobalt compound alternatively into an organic phase by the organic solvent containing alkyl phosphoric acid The approach (Japanese-Patent-Application-No. No. 268881 [seven to] official report) of carrying out solid liquid extraction of the cobalt compound alternatively to the bottom of heating stirring etc. is mentioned by the emulsion extractant of JP,5-14013,B and the organic solvent-water-hydrogen-peroxide (water-soluble reducing agent) system containing alkyl phosphoric acid. It is the solvent extraction approach that solvent extraction recovers cobalt preferably.

[0028] As alkyl phosphoric acid used for extracting a cobalt compound by this solvent extraction approach, it is dialkyl phosphoric acid, such as alkyl phosphonic acid monoalkyl ester, such as 2-ethylhexyl phosphonic acid Monod 2-ethylhexyl ester (M2EHFA), and phosphoric acid screw-2-ethylhexyl (D2EHFA), and phosphoric acid screw-2-dodecyl, and six or more things are mentioned for the carbon number of an alkyl group, for example.

[0029] In addition, about the remaining roast ash which sorted out the cobalt inclusion by the magnetic separation of this invention, since it contains metals, such as copper, in abundance, these metals may be collected by approaches, such as electrolytic refining, as occasion demands.

[0030]

[Embodiment of the Invention] Hereafter, according to the flow chart shown in an accompanying drawing, the gestalt of the suitable operation about the cobalt recovery approach from the rechargeable battery useless article of this invention is explained.

[0031] first, equipments, such as an electric furnace and a gas furnace, -- using -- a cell useless article -- the temperature of 600 degrees C or more -- it roasts over 700-900 degrees C preferably for 1 to 3 hours. As for

the cobalt compound in a cell useless article, that part is returned to metal cobalt by this roast processing, and other cobalt compounds are considered to exist in the condition that it adhered or adsorbed by this metal cobalt as cobalt oxide in that case.

[0032] next, the roast cell obtained at the roast process -- neglect cooling -- or forced cooling is carried out, and it cools to a room temperature, and judges in magnitude of 3-10mm with cutters, such as shredder. And the decision object of the roast cell obtained at the decision process is sifted out by a metal scrap and the roast ash on the conditions which use a vibration screen etc. next and can do 20 meshes a screen exception preferably.

[0033] About the roast ash obtained at this sieving process, the magnetic separation of the cobalt inclusion which uses metal cobalt and cobalt oxide as a principal component using an electromagnet etc., the other metal, and its oxide are carried out to the residual ash with which it is mainly concerned. the rate which carries out magnetic separation as a cobalt inclusion here -- desirable -- the roast ash in front of magnetic separation -- receiving -- a weight ratio -- it is [0.6 or less] good that it is 0.5 or less more preferably, and the metal cobalt and the cobalt oxide in a roast ash are condensed by twice [1.6 to / more than] as many concentration as this as a result.

[0034] The cobalt inclusion sorted out at the magnetic separation process is dissolved in mineral acids, such as a hydrochloric acid and a sulfuric acid, next (acid dissolution process), subsequently, in an organic phase, liquid-liquid extraction of the cobalt compound in an acid solution is carried out alternatively, and it is recovered by the organic solvent containing alkyl phosphoric acid.

[0035] After carrying out roast processing of the rechargeable battery useless article and carrying out decision processing subsequently in this invention, a metal scrap and a roast ash A screen analysis opium poppy, Since it considers as the cobalt inclusion which sorts out the obtained roast ash with a magnet at a magnetic separation process, and contains metal cobalt and cobalt oxide in high concentration, acid dissolution processing and solvent extraction processing are performed subsequently to this cobalt inclusion and cobalt is collected The amount of the acid used needed by acid dissolution processing can be reduced as much as possible, and also the recovery effectiveness of cobalt can be made to improve.

[0036]

[Example] Hereafter, based on an example and the example of a comparison, this invention approach is explained concretely.

[0037] This was put into the core of an annular electric furnace using one useless article of a cylindrical rechargeable lithium-ion battery with a weight of 35.93g by phix65mm with example 1 dimension of 18mm, and it roasted over 800 degrees C for 2 hours.

[0038] Thus, the roast cell obtained by carrying out roast processing was cut out in magnitude of about 10mm using the cutter, and the obtained decision object was sifted out and carried out using the vibration screen of 16 meshes. This sieving classified pieces of decision, such as a piece of iron of the cell container origin, a piece of copper foil of the negative-electrode material origin, and a piece of aluminum foil of the positive-electrode material origin, to metal scrap 14.38g of a plus sieve, and roast ash 16.81g of a minus sieve made into a subject.

[0039] Magnetic separation were carried out to 14.57g of cobalt inclusions which stick to this electromagnet using an electromagnet about roast ash 16.81g obtained by the above-mentioned sieving processing, and the other residual ash 2.24g which does not stick to this electromagnet, and cobalt inclusions were collected. The cobalt inclusion collected by this magnetic separation processing is the weight ratio 0.87 to the roast ash in front of magnetic separation, and the metal cobalt and the cobalt oxide in a roast ash were condensed 1.15 times.

[0040] Next, 14.57g of cobalt inclusions obtained by doing in this way was dissolved and filtered using 186ml of mixed acids of the weight ratio 2:1 of the hydrochloric acid of 10 % of the weight of concentration, and the nitric acid of 10 % of the weight of concentration, separation removal of the 4.61g of the insoluble matter was carried out, and the acid melt was obtained.

[0041] After having adjusted the obtained acid melt to pH6 using the sodium-hydroxide water solution 10% of the weight, settling as a hydroxide the ion of the iron currently mixed as an impurity, aluminum, and copper and filtering and removing, the obtained filtrate is adjusted to pH10, cobalt hydroxide was settled, sediment of this cobalt hydroxide was filtered, collected and dried, and 10.78g of cobalt hydroxide was obtained. 10.78g of this cobalt hydroxide was heated at 500 degrees C among the hydrogen air current for 1 hour, it returned and metal cobalt 6.84g was obtained. The purity of the obtained metal cobalt was 99.3%, and the cobalt recovery over all the cobalt contained in the cell useless article was 87.8%.

[0042] When it was made to dissolve in the mixed acid (weight ratio 2:1 of the hydrochloric acid of 10 % of

the weight of concentration, and the nitric acid of 10 % of the weight of concentration) used in the example 1 as it was, without carrying out the magnetic separation of the roast ash 16.81g obtained in the example of comparison 1 above-mentioned example 1 at a magnetic separation process, 221ml of mixed acids was needed, and it filtered and separation recovery of the 4.90g of the insoluble matter was carried out. The obtained acid melt was processed like the above-mentioned example 1, and metal cobalt was collected. The purity of the obtained metal cobalt was 85.9%, and the cobalt recovery over all the cobalt contained in the cell useless article was 87.1%.

[0043]

[Effect of the Invention] According to this invention, the cobalt of a rare metal can be efficiently collected from the cell useless article of a rechargeable battery using a small amount of as much as possible acid, and industrial value is high.

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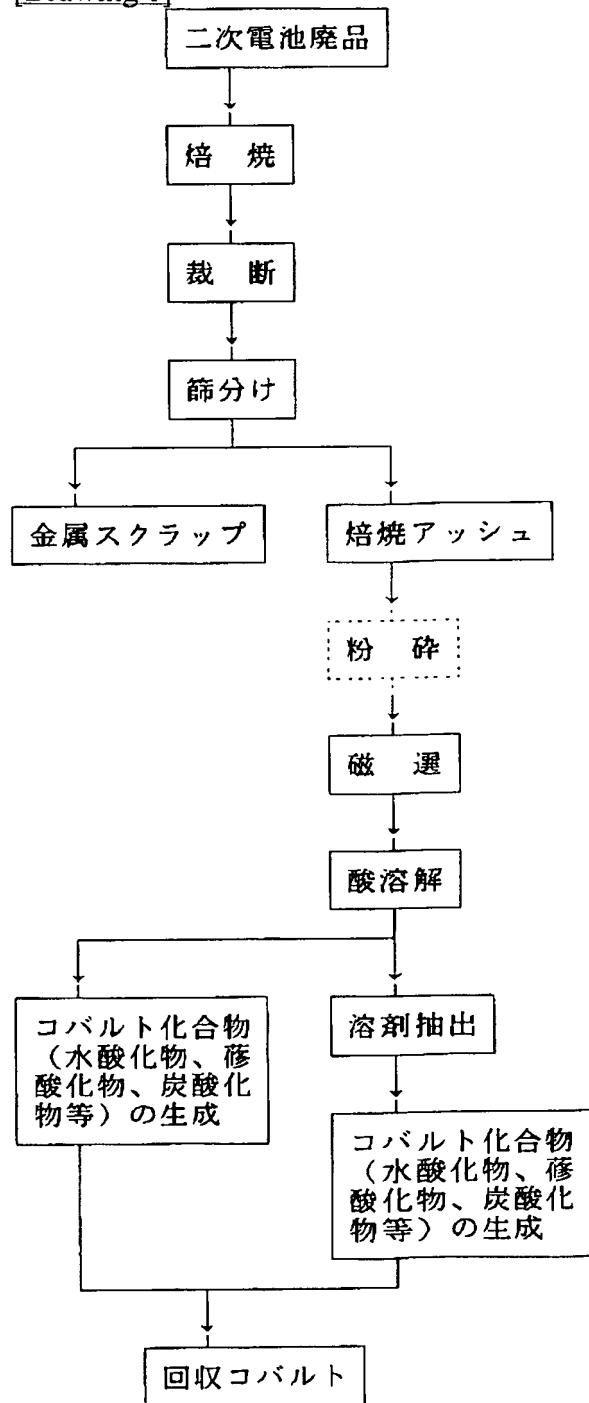
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DRAWINGS

[Drawing 1]



[Translation done.]

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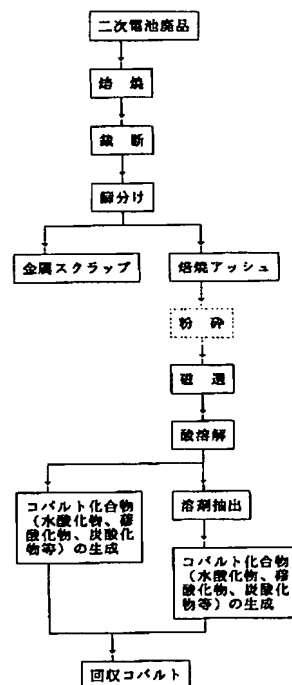
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(54) 【発明の名称】 二次電池廃品からのコバルト回収方法

(57) 【要約】

【課題】 二次電池の電池廃品から希少金属のコバルトを、可及的少量の酸を用いて効率良く回収することができる二次電池廃品からのコバルト回収方法を提供する。

【解決手段】 電極材中にコバルトを含む二次電池の電池廃品を600℃以上の温度で焙焼する焙焼工程と、この焙焼工程で得られた焙焼電池を裁断する裁断工程と、この裁断工程で得られた焙焼電池の裁断物を篩分けて金属スクラップと焙焼アッシュとに分離する篩分け工程と、この篩分け工程で得られた焙焼アッシュ中から磁石を用いてコバルト含有物を磁気分離する磁選工程と、この磁選工程で選別されたコバルト含有物を酸に溶解する酸溶解工程と、この酸溶解工程で得られた酸溶解物からコバルトを回収する回収工程とを含む二次電池廃品からのコバルト回収方法である。



【特許請求の範囲】

【請求項1】 電極材中にコバルトを含む二次電池の電池廃品を600℃以上の温度で焙焼する焙焼工程と、この焙焼工程で得られた焙焼電池を裁断する裁断工程と、この裁断工程で得られた焙焼電池の裁断物を篩分けて金属スクラップと焙焼アッシュとに分離する篩分け工程と、この篩分け工程で得られた焙焼アッシュ中から磁石を用いてコバルト含有物を磁気分離する磁選工程と、この磁選工程で選別されたコバルト含有物を酸に溶解する酸溶解工程と、この酸溶解工程で得られた酸溶解物からコバルトを回収する回収工程とを含むことを特徴とする二次電池廃品からのコバルト回収方法。

【請求項2】 回収工程が、溶剤抽出によりコバルトを回収する溶剤抽出工程である請求項1に記載の二次電池廃品からのコバルト回収方法。

【請求項3】 焙焼工程での電池廃品の焙焼は、密閉容器中又は還元雰囲気中で700～900℃の温度で行う請求項1又は2に記載の二次電池からのコバルト回収方法。

【請求項4】 篩分け工程で得られた焙焼アッシュは、磁選工程で磁選される前に所定の粒度に粉碎される請求項1～3の何れかに記載の二次電池廃品からのコバルト回収方法。

【請求項5】 焙焼アッシュは、平均粒度2mm以下に粉碎されている請求項1～4の何れかに記載の二次電池廃品からのコバルト回収方法。

【請求項6】 磁選工程での焙焼アッシュの磁選は、湿式磁気分離により行う請求項1～5の何れかに記載の二次電池廃品からのコバルト回収方法。

【請求項7】 磁選工程で選別されたコバルト含有物は、磁選前の焙焼アッシュに対して重量比0.6以下である請求項1～6の何れかに記載の二次電池廃品からのコバルト回収方法。

【請求項8】 電極材中にコバルトを含む二次電池の電池廃品を600℃以上の温度で焙焼する焙焼工程と、この焙焼工程で得られた焙焼電池を裁断する裁断工程と、この裁断工程で得られた焙焼電池の裁断物を磁石により磁性体と非磁性体とに磁気分離する磁選工程と、この磁選工程で得られた磁性体を篩分けて磁性金属スクラップとコバルト含有物とに分離する篩分け工程と、この篩分け工程で得られたコバルト含有物を酸に溶解する酸溶解工程と、この酸溶解工程で得られた酸溶解物からコバルトを回収する回収工程とを含むことを特徴とする二次電池廃品からのコバルト回収方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、二次電池の製造工程で発生する不良品や使用済み二次電池の回収品等の電池廃品からその電極材に含まれる希少金属のコバルトを効率的に回収することができる二次電池廃品からの

コバルト回収方法に関する。

【0002】

【従来の技術】例えば、リチウムイオン二次電池にはその正極材としてリチウム酸コバルト (LiCoO_2) が用いられており、また、ニッケル水素電池にはその正極材の活物質である水素化ニッケル中に容量利用率向上を目的として酸化コバルトが添加されており、更に、ニカド電池にはその正極材 (ニッケル) 中に耐腐蝕性向上や高容量化を目的として硝酸コバルトが添加されている。

【0003】そして、このような正極材は、例えばリチウムイオン二次電池の場合には、炭酸リチウムと酸化コバルトとを混合し、焼成してリチウム酸コバルトとし、次いでこのリチウム酸コバルトとアセチレンブラックやカーボン等の導電剤及びフッ素樹脂、フッ素ゴム等の結着剤とを配合し、これを有機溶剤によりスラリー状に混練し、この混練物をアルミニウム箔 (以下、単に「アルミ箔」という) 等の金属箔上に均一に塗布し、乾燥して溶剤を除去し、金属箔に導電剤2～10重量%及び結着剤2～10重量%が塗着され、これを所定の形状に裁断することにより形成されている。

【0004】ところで、このような二次電池は、ノート型パソコン、携帯電話、簡易携帯電話 (PHS)、電気シェーバー、ヘッドホンステレオ、VTR等のポータブル電気機器の普及に伴って需要が急速に高まり、その生産量が増加するにつれ、この二次電池の製造時に発生する不良品や使用済み二次電池の回収品等の電池廃品の量が飛躍的に増加し、これら電池廃品の処理が問題になってきている。

【0005】その一方で、コバルトは資源に乏しく、我が国ではそのほとんどを外国に依存しているにもかかわらず、その用途は二次電池の電極材、顔料、窯業、フェライト、触媒、超硬合金等の日用品からハイテク製品に至るまで極めて広範に亘っており、特にリチウムイオン二次電池にはその1個当たり酸化コバルトとして約7gも使用されている。このため、コバルトは元々高価であると共にその需要が増大して益々高価になりつつある。

【0006】このため、従来においても、例えば超硬合金や触媒の廃棄物を酸溶解処理し、得られたコバルト及びニッケルを含む酸溶解液からアルキル磷酸を含む抽出剤でこの抽出剤中にコバルトイオンを選択的に抽出し、更に得られた抽出液をシュウ酸水溶液と接触させてシュウ酸コバルトを析出させて回収することにより、コバルト及びニッケルを含む溶液から高純度でコバルトを回収する方法が提案されている (特公平5-14013号公報)。

【0007】

【発明が解決しようとする課題】そこで、上述した電池廃品についても、これを粉碎して塩酸や硝酸等の鉱酸で溶解し、不溶性のアセチレンブラックやカーボン等の導電剤やフッ素樹脂、フッ素ゴム等の結着剤等を分離除去

し、コバルトを始めとするリチウム、アルミニウム等の金属を含む酸溶解液を回収し、この酸溶解液からアルキル磷酸を含む抽出剤でコバルトを選択的に回収することが検討されている。

【0008】しかしながら、この方法においては、酸溶解液中には単に電池廃品中のコバルトやリチウム等の金属化合物が溶解するだけでなく、金属箔のアルミニウム等も含めて溶解するので、電池廃品の量が増加するに連れてこの酸溶解処理に要する酸、例えば塩酸や硝酸等の使用量が大幅に増加し、この酸溶解液から抽出剤でコバルトイオンを抽出した後の酸廃液が大量に生じ、この大量の酸廃液の処理に水酸化ナトリウム等の大量のアルカリが必要になってかえって廃液処理に多大な問題が発生するほか、酸として塩酸を使用すると酸溶解処理時に塩素ガスが大量に発生し、また、硝酸を使用すると酸溶解処理時に亜硝酸ガスが大量に発生し、これらの酸性排ガスの処理にも多大な費用を要するという問題もある。

【0009】また、先ず始めに電池廃品中のアルミ箔等の金属箔や一部のリチウム化合物等を水酸化ナトリウム等のアルカリに溶解して除去し、次に残された正極材中のコバルト化合物等の他の金属化合物、導電剤、結着剤等を塩酸等の鉱酸で酸溶解処理し、可溶性の正極材と導電剤や結着剤とを分離し、コバルトやリチウム等の金属を含む酸溶解液を得てアルキル磷酸を含む抽出剤でコバルトを選択的に回収する方法も考えられる。

【0010】しかしながら、この方法においては、酸浸出処理とは別にアルカリによる金属箔を分離除去するためのアルカリ前処理が必要になって工程が複雑化し、更にはこれらアルカリ前処理や酸浸出処理で用いたアルカリ廃液や酸廃液が大量に発生し、上記と同様に、廃液処理に多大な問題が発生するほか、酸浸出処理時における酸性排ガス問題も残る。

【0011】更に、特開平3-10032号公報には、アルキル磷酸を含む有機溶液を水の存在下で用いることにより、コバルト及びニッケル酸化物からコバルトを選択的に直接溶液抽出する方法が開示されている。

【0012】しかしながら、この方法においても、正極材中でコバルト化合物等の金属化合物が導電剤や結着剤で被覆されており、この導電剤や結着剤の存在が障害になって、アルキル磷酸を含む有機溶液-水系の抽出剤がコバルト化合物と効率的に接触できず、この抽出剤による抽出効率が高くても30~40重量%程度と低く、到底工業的に実施できる値ではない。

【0013】そこで、本発明者らは、電池廃品から希少金属のコバルトを如何に分離して回収するかについて鋭意研究を重ねた結果、電池廃品を600℃以上で焙焼処理し、次いで裁断し、篩分けして得られた焙焼アッシュを磁石を用いて金属コバルト及びコバルト酸化物を主成分とするコバルト含有物を磁選し、得られたコバルト含有物を酸溶解処理して溶剤抽出処理することにより、電

池廃品中のコバルトを大量の酸を使用することなく、しかも、効率良くコバルトを回収できることを見出し、本発明を完成した。

【0014】従って、本発明の目的は、二次電池の電池廃品から希少金属のコバルトを、可及的少量の酸を用いて効率良く回収することができる二次電池廃品からのコバルト回収方法を提供することにある。

【0015】

【課題を解決するための手段】すなわち、本発明は、電極材中にコバルトを含む二次電池の電池廃品を600℃以上の温度で焙焼する焙焼工程と、この焙焼工程で得られた焙焼電池を裁断する裁断工程と、この裁断工程で得られた焙焼電池の裁断物を篩分けて金属スクラップとコバルト含有物を含む焙焼アッシュとに分離する篩分け工程と、この篩分け工程で得られた焙焼アッシュ中から磁石を用いてコバルト含有物を磁気分離する磁選工程と、この磁選工程で選別されたコバルト含有物を酸に溶解する酸溶解工程と、この酸溶解工程で得られた酸溶解物からコバルトを回収する回収工程とを含む二次電池廃品からのコバルト回収方法である。

【0016】また、本発明は、電極材中にコバルトを含む二次電池の電池廃品を600℃以上の温度で焙焼する焙焼工程と、この焙焼工程で得られた焙焼電池を裁断する裁断工程と、この裁断工程で得られた焙焼電池の裁断物を磁石により磁性体と非磁性体とに磁気分離する磁選工程と、この磁選工程で得られた磁性体を篩分けて磁性金属スクラップとコバルト含有物とに分離する篩分け工程と、この篩分け工程で得られたコバルト含有物を酸に溶解する酸溶解工程と、この酸溶解工程で得られた酸溶解物からコバルトを回収する回収工程とを含む二次電池廃品からのコバルト回収方法である。

【0017】本発明方法において、コバルト回収の対象となる二次電池廃品は、二次電池の製造時に発生する不良品や使用済み二次電池の回収品等であり、電極材中にコバルトを含むものである。この電極材中にコバルトを含む二次電池としては、代表的には例えば、その正極材中に酸化コバルトや硝酸コバルト等のコバルト化合物等を含むリチウムイオン二次電池、ニッケル水素電池、ニカド電池等を挙げることができる。

【0018】本発明方法においては、先ずこのように電極材中にコバルトを含む二次電池の電池廃品を600℃以上、好ましくは700~900℃の温度で通常1~3時間程度焙焼する。この電池廃品の焙焼工程での焙焼処理は、好ましくは密閉容器中あるいは還元雰囲気中で行われ、磁選工程で金属コバルト及びコバルト酸化物を主成分とするコバルト含有物を効率良く磁気分離するために少なくとも電極材中のコバルト化合物の一部が還元されて金属コバルトとなる必要がある。ここで、焙焼温度が600℃より低いと、得られる焙焼アッシュ中のコバルト含有物中における金属コバルトの量が少なくなり、

磁選工程で効率良くコバルト含有物を磁気分離するのが困難になる。また、焙焼温度が900℃を超えても、磁選工程でのコバルト含有物の選別には特に問題はないが、焙焼工程でのエネルギーコストが嵩み、工業的に実施するのに好ましくない。

【0019】この焙焼工程では、例えば電池廃品の正極材中のコバルト酸化物（例えば、 Co_2O_3 ）がこの電池廃品中のアルミニウム（Al）やカーボン（C）等を還元剤として還元され、その一部が完全に還元されて磁性体の金属コバルト（Co）に変換すると共に、部分的

に還元されて生成した酸化コバルト（ Co_3O_4 ）はこの金属コバルトと共に存在すると考えられる。

【0020】上記焙焼工程で得られた焙焼電池は次に裁断機で裁断されて裁断物となり、この焙焼電池の裁断物中には、鉄、アルミニウム、ステンレス等の金属で形成された電池の外側容器や、アルミ箔、銅箔等の金属箔で形成された集電体等に由来する比較的大きな裁断片の金属スクラップと、集電体に塗着されていたコバルト化合物等の金属化合物、アセチレンブラックやカーボン等の導電剤及びフッ素樹脂、フッ素ゴム等の結着剤等の正極材や負極材、ポリエチレン多孔膜等で形成されたセパレータ等の有機物質等に由来する金属コバルトやコバルト酸化物その他の金属やその酸化物、カーボン等からなる比較的小さな粉末状あるいは顆粒状の焙焼アッシュとが存在する。

【0021】そして、上記裁断工程で得られた焙焼電池の裁断物は、先に篩分け工程で比較的大きな裁断片の金属スクラップと比較的小さな粉末状あるいは顆粒状の焙焼アッシュとに篩分けられて分離され、次いで磁選工程で磁性体のコバルト含有物が選別されるか、あるいは、先に磁選工程で磁石により磁性体と非磁性体とに選別され、次いで篩分け工程で磁性体を篩分けて磁性金属スクラップとコバルト含有物とに分離されるが、磁選工程での処理量を低減すると共に金属スクラップと焙焼アッシュとをより完全に分離するために、好ましくは前者の先に篩分けを行ってから磁選する方法である。

【0022】上記篩分け工程では、好ましくは振動篩が用いられ、金属スクラップに付着した焙焼アッシュが可及的に除去され、回収された金属スクラップ、例えば鉄、ステンレス、アルミニウム、銅は再資源化して有効利用される。また、上記磁選工程では、特に制限されるものではないが、例えばドラム型湿式分離機やベルト型湿式分離機、更には種々のタイプの乾式分離機等の装置を用い、磁性物質と非磁性物質との付着時間の差を利用して磁気分離が行われる。

【0023】ここで、篩分け工程で得られた焙焼アッシュについては、これを磁選工程に移送する前に、必要によりボールミル等の粉碎機で粉碎処理し、この焙焼アッシュの粒度を平均粒度2mm以下、好ましくは1.65mm（12メッシュ）以下、より好ましくは1.16

8mm（16メッシュ）以下に粉碎するのがよい。このように焙焼アッシュを平均粒度2mm以下に粉碎することにより、金属コバルト及びコバルト酸化物を比較的高濃度に含む粉体とコバルト以外の金属及びその酸化物を比較的高濃度に含む粉体とに分かれ、磁選工程で比較的高濃度に金属コバルト及びコバルト酸化物を含むコバルト含有物が得られる。

【0024】篩分け工程から磁選工程を経て、あるいは、磁選工程から篩分け工程を経て得られたコバルト含有物は、焙焼電池を裁断して生じた磁選前の焙焼アッシュに対して、その重量が少しでも減少していれば、後の酸溶解処理で必要とする酸の使用量がそれだけ減少することになり、酸溶解工程で使用する酸の量を減少せしめる効果が得られるが、この酸溶解工程で使用する酸の量は可及的に減少せしめるのがよく、また、工業的に実施する上で、好ましくは磁選前の焙焼アッシュに対して重量比0.6以下、より好ましくは0.5以下にするのがよい。

【0025】この磁選工程で得られたコバルト含有物は、金属コバルト及びコバルト酸化物を主成分とするものであるが、これら以外に、例えば金属コバルトと焼結した銅やアルミニウム等の金属やその酸化物を相当の割合で含有する。このコバルト含有物中における金属コバルト及びコバルト酸化物の合計の含有割合（以下、これを単に「コバルト含有率」という）は、通常20重量%以上、好ましくは40重量%以上であるのがよい。このコバルト含有率は、高ければ高いほど、単位コバルト量に対して必要とされる酸の量が減少し、酸溶解工程での酸の使用量が減少する。

【0026】本発明において、磁選工程で得られたコバルト含有物は、次に塩酸、硫酸、硝酸等の適当な酸を用いて溶解し、酸溶解物とされる（酸溶解工程）。この酸溶解工程で用いられる酸としては、典型的には塩酸や硫酸等の鉱酸が挙げられ、その使用量は通常コバルト含有物1モルに対して1～3モルの範囲である。

【0027】酸溶解工程で得られた酸溶解物は、次にコバルトを回収するための回収工程に移送される。この回収工程については、それが酸溶解物からコバルトを選択的に回収できる工程であればよく、例えば、pH調整によりコバルト化合物以外の金属化合物を可及的に分離除去した後、pH10に調整して水酸化コバルトを析出させ、この水酸化コバルトを還元雰囲気中で還元して金属コバルトとして回収する方法や、アルキル磷酸を含む有機溶剤で有機相中にコバルト化合物を選択的に液液抽出する方法（特公昭56-11371号公報、特公平5-14013号公報）や、アルキル磷酸を含む有機溶剤—水—過酸化水素（水溶性還元剤）系のエマルジョン抽出剤で加熱攪拌下にコバルト化合物を選択的に固液抽出する方法（特願平7-268881号公報）等が挙げられ、好ましくは溶剤抽出によりコバルトを回収する溶剤

抽出方法である。

【0028】この溶剤抽出方法でコバルト化合物を抽出するのに用いられるアルキル磷酸としては、例えば、2-エチルヘキシルホスホン酸モノ-2-エチルヘキシルエステル (M2EHPA) 等のアルキルホスホン酸モノアルキルエステル、及び、磷酸ビス-2-エチルヘキシル (D2EHPA)、磷酸ビス-2-ドデシル等のジアルキル磷酸であって、アルキル基の炭素数が6以上のものが挙げられる。

【0029】なお、本発明の磁選によりコバルト含有物を選別した残りの焙焼アッシュについては、それが銅等の金属を豊富に含むものであるから、必要により、例えば電解精錬等の方法でこれらの金属を回収してもよい。

【0030】

【発明の実施の形態】以下、添付図面に示すフローチャートに従って、本発明の二次電池廃品からのコバルト回収方法についての好適な実施の形態を説明する。

【0031】まず、電気炉やガス炉等の装置を用い、電池廃品を600℃以上の温度、好ましくは700～900℃で1～3時間焙焼する。この焙焼処理により、電池廃品中のコバルト化合物はその一部が金属コバルトに還元され、その際に他のコバルト化合物はコバルト酸化物としてこの金属コバルトに付着あるいは吸着されたような状態で存在すると考えられる。

【0032】次に、焙焼工程で得られた焙焼電池を放置冷却あるいは強制冷却して室温まで冷却し、シュレッダー等の裁断機で例えば3～10mmの大きさに裁断する。そして、裁断工程で得られた焙焼電池の裁断物は、次に振動篩等を用いて好ましくは20メッシュを篩別できる条件で金属スクラップと焙焼アッシュとに篩分けられる。

【0033】この篩分け工程で得られた焙焼アッシュについては、電磁石等を用いて金属コバルト及びコバルト酸化物を主成分とするコバルト含有物とそれ以外の金属及びその酸化物を主とする残留アッシュとに磁気分離する。ここで、コバルト含有物として磁気分離する割合は、好ましくは磁選前の焙焼アッシュに対して重量比0.6以下、より好ましくは0.5以下であるのがよく、結果として焙焼アッシュ中の金属コバルト及びコバルト酸化物は1.6～2倍以上の濃度に濃縮される。

【0034】磁選工程で選別されたコバルト含有物は、次に塩酸や硫酸等の鉱酸に溶解され（酸溶解工程）、次いで酸溶解液中のコバルト化合物はアルキル磷酸を含む有機溶剤で有機相中に選択的に液液抽出され、回収される。

【0035】本発明においては、二次電池廃品を焙焼処理し、次いで裁断処理したのち金属スクラップと焙焼アッシュとを篩分けし、得られた焙焼アッシュを磁選工程で磁石により選別して金属コバルト及びコバルト酸化物を高濃度を含むコバルト含有物とし、次いでこのコバル

ト含有物に酸溶解処理と溶剤抽出処理を施してコバルトの回収を行うので、酸溶解処理で必要とする酸の使用量を可及的に低減することができるほか、コバルトの回収効率を向上せしめることができる。

【0036】

【実施例】以下、実施例及び比較例に基づいて、本発明方法を具体的に説明する。

【0037】実施例1

外形寸法18mmφ×65mmで重量35.93gの円筒型のリチウムイオン二次電池の廃品1個を用い、これを環状の電気炉の中心部に入れて800℃で2時間焙焼した。

【0038】このように焙焼処理して得られた焙焼電池を、裁断機を用いて約10mmの大きさに裁断し、得られた裁断物を16メッシュの振動篩を用いて篩分けした。この篩分けにより、電池容器由来の鉄片や負極材由来の銅箔片、正極材由来のアルミ箔片等の裁断片を主体とする篩上の金属スクラップ14.38gと篩下の焙焼アッシュ16.81gとに分別した。

【0039】上記篩分け処理により得られた焙焼アッシュ16.81gについて、電磁石を用い、この電磁石に吸着するコバルト含有物14.57gとこの電磁石には吸着しないそれ以外の残留アッシュ2.24gとに磁気分離し、コバルト含有物を回収した。この磁選処理で回収されたコバルト含有物は、磁選前の焙焼アッシュに対して重量比0.87であり、焙焼アッシュ中の金属コバルト及びコバルト酸化物は1.15倍に濃縮された。

【0040】次に、このようにして得られたコバルト含有物14.57gを、濃度10重量%の塩酸と濃度10重量%の硝酸の重量比2:1の混酸186mlを用いて溶解し、濾過して不溶物4.61gを分離除去し、酸溶解物を得た。

【0041】得られた酸溶解物を10重量%水酸化ナトリウム水溶液を用いてpH6に調整し、不純物として混入している鉄、アルミニウム、銅のイオンを水酸化物として沈殿させ、濾過して除去したのち、得られた濾液をpH10に調整して水酸化コバルトを沈殿させ、この水酸化コバルトの沈殿物を濾過して回収し、乾燥させて水酸化コバルト10.78gを得た。この水酸化コバルト10.78gを水素気流中500℃で1時間加熱し、還元して金属コバルト6.84gを得た。得られた金属コバルトの純度は99.3%であり、電池廃品中に含まれていた全コバルトに対するコバルト回収率は87.8%であった。

【0042】比較例1

上記実施例1で得られた焙焼アッシュ16.81gを磁選工程で磁気分離することなくそのまま実施例1で用いた混酸（濃度10重量%の塩酸と濃度10重量%の硝酸の重量比2:1）に溶解させたところ、混酸221mlを必要とし、また、濾過して不溶物4.90gが分離回

収された。得られた酸溶解物を上記実施例 1 と同様にして処理して金属コバルトの回収を行った。得られた金属コバルトの純度は 85.9% であり、電池廃品中に含まれていた全コバルトに対するコバルト回収率は 87.1% であった。

【0043】

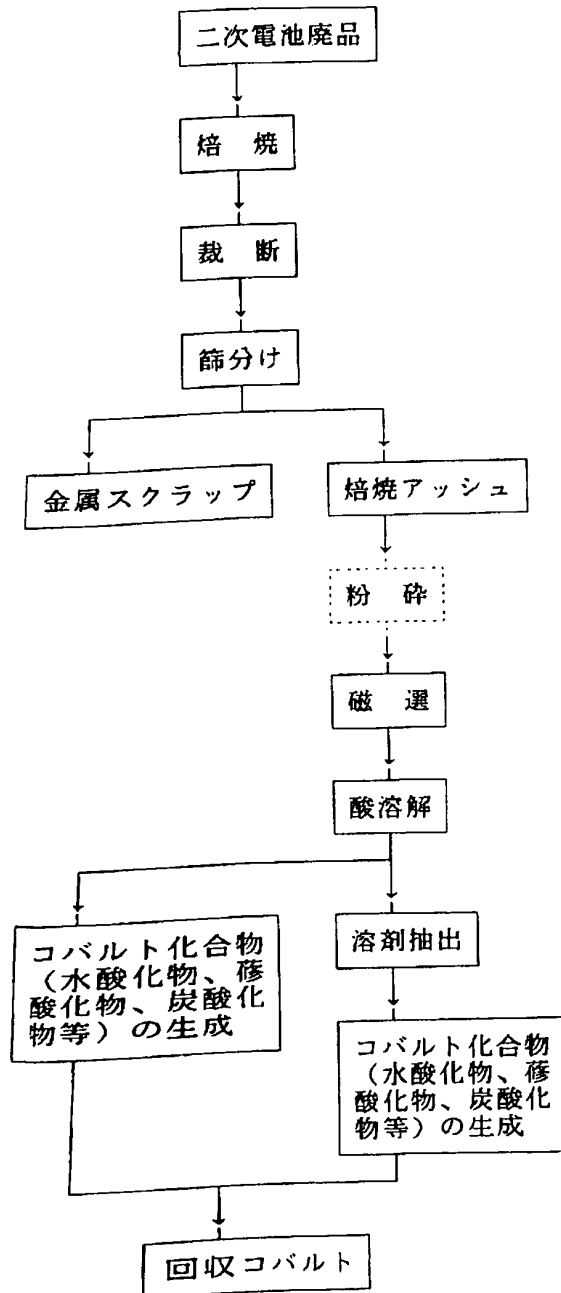
【発明の効果】本発明によれば、可及的少量の酸を用い*

*て、二次電池の電池廃品から希少金属のコバルトを効率良く回収することができ、工業的価値の高いものである。

【図面の簡単な説明】

【図 1】 図 1 は、本発明の好適な実施形態に係る二次電池廃品からのコバルト回収方法を示すフローチャートである。

【図 1】



フロントページの続き

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